

Pt-Doped Hematite Thin Films May Enable Solar-Powered Generation of Hydrogen

While today's debate over renewable energy sources has focused a great deal of attention on using sunlight to generate electricity, the possibility of solar-powered hydrogen generation is less well known to the public. However, a recent materials advance has brought the technology to derive hydrogen and other chemicals using sunlight one step closer to reality, and may eventually shift the contours of the energy debate. Y.-S. Hu, E.W. McFarland, and their colleagues at the University of California at Santa Barbara have synthesized a doped hematite material with significantly improved characteristics for harnessing sunlight to split water into oxygen and hydrogen. They reported their findings in the June 24 issue of *Chemistry of Materials* (DOI: 10.1021/cm800144q; p. 3803).

First demonstrated over 30 years ago, photoelectrochemical (PEC) electrolysis of water uses the electron-hole pairs liberated by the illumination of a semiconductor to drive oxidation-reduction reactions, releasing oxygen and hydrogen. The search has since been on for a semiconductor material that would enable high-efficiency solar-powered PEC electrolysis. Hematite ($\alpha\text{-Fe}_2\text{O}_3$) has been extensively studied as a candidate material because of its relatively narrow bandgap (2.0–2.2 eV), good stability in several common electrolytes, safety, and low cost. However, the major limitations of pure hematite include its relatively low conductivity and its high electron-hole recombination rate. A number of studies have focused on introducing dopants, including Pt, to hematite in an

effort to improve its PEC performance.

Despite previous unfavorable results by other researchers, the UC Santa Barbara team decided to investigate Pt-doped hematite for PEC applications. Using an electrodeposition technique, which had not previously been studied for synthesis of doped hematite, the team prepared samples of Pt-doped iron hydroxides, which they then calcined at 700°C for 4 h to obtain doped crystalline hematite thin films. Scanning electron micrographs of the films showed a dramatic change in their morphology in the presence of a dopant molar ratio of 2–10% Pt in the electrolyte, to a much more uniform and dense structure than undoped samples. X-ray diffraction and x-ray photoelectron spectroscopy revealed that the doped thin films remained in a rhombohedral lattice with a fairly constant Pt concentration throughout the sample. The researchers found that when illuminated, the doped thin films showed significantly increased photocurrent generation (a measure of hydrogen production) compared with undoped hematite thin films, implying that a PEC electrolysis device built with these samples would display an overall energy efficiency of up to 3%, nearly four times greater than devices relying on undoped hematite.

While questions remain about the precise mechanism of the improvement of the PEC process from the Pt dopant and a bias is still required, this result suggests that cost-effective solar-powered generation of hydrogen and other chemicals using abundant and non-toxic materials may one day be feasible.

COLIN MCCORMICK

Superhard Diamondlike BC₅ Predicted to Be a High-T_c Superconductor

Although boron-doped diamond ($\text{B}_8\text{C}_{1-\delta}$ with $\delta = 0.028$) is superconducting with a critical temperature (T_c) of 7 K, other carbon materials, such as intercalated graphite, nanotubes, and alkali-doped fullerides, have substantially higher T_c values, ranging from 11–33 K. Superhard nanocrystalline BC₅ aggregates, with an effective δ of 0.167, were recently synthesized. The BC₅ crystal structure shows cubic symmetry with volume per atom (6.00 \AA^3) 6% larger than diamond. However, the B and C atoms cannot be distinguished by diffraction (because of their similar atomic number), so that the position of the B atom in the cell is undetermined. While calculations based upon density functional theory (DFT) have shown that superconductivity in B-doped diamond (at low B content) is mediated by B-phonon states, it has been unclear whether superconductivity could scale with the doping level up to $\delta = 0.167$. Recently, M. Calandra and F. Mauri at CNRS and Institut de Minéralogie et de Physique des Milieux condensés, Paris, France, used DFT to resolve the BC₅ crystal structure and to predict that BC₅ is superconducting with a $T_c = 45 \text{ K}$, which is larger than the T_c for MgB₂, experimentally found to be 39 K.

As reported in the July 4 issue of *Physical Review Letters* (DOI: 10.1103/PhysRevLett.101.016401; 016401), Calandra and Mauri replaced one of the two C atoms in the diamond cell with a B atom and performed volume and force optimizations on the 6-atom hexagonal supercell. The most

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stable structure is nonmagnetic, has a volume per atom 5.2% larger than in diamond (in good agreement with experiment), and shows a slight elongation of the cubic cell along the (111) axis. The researchers found this configuration to be the most stable after considering all possible positions for two B atoms in a 12-atom supercell. The density of states at the Fermi level for BC_5 was found to be two times larger than for B-doped diamond with $\delta = 0.028$, showing that the number of carriers does not saturate even at $\delta = 0.167$. The average electron-phonon coupling for BC_5 is approximately 0.89, which is comparable to the coupling for MgB_2 . The researchers' analysis showed that the dominant contribution to the electron-phonon coupling comes from the vibrations of the B-C bonds. The researchers said that the large elastic constants in superhard materials require short, strong chemical bonds (typical of materials composed of light elements) that result in energetic phonons. Doping sufficient to sustain moderate electron-phonon coupling results in high- T_c superconductivity. Noting that the grain size of the BC_5 aggregates is only 10–15 nm and that bulk superconductivity is possible only if the coherence length is at least comparable to the size of the grains, Calandra and Mauri said that "it is necessary to grow larger samples, possibly by longer synthesis or by the use of catalysts to speed up the reaction."

STEVEN TROHALAKI

Spin-Polarized Excitonic Photoluminescence Observed in Mn^{2+} -Doped Colloidal CdSe Quantum Dots

Colloidal transition-metal-doped semiconductor nanocrystals have been attracting interest in spintronics, bioimaging, and other fields. However, an undesirable side effect of metal-ion doping is that it often leads to quenching of excitons by energy transfer to the dopants followed by nonradiative recombination. R. Beaulac of the University of Washington, X. Liu of the University of Notre Dame, S. Lee of Korea University, and their co-workers have now reported that the excitonic emission of Mn^{2+} -doped CdSe nanocrystals can be retained and co-exists with strong dopant-exciton magnetic exchange coupling by using quantum confinement to tune the CdSe excitonic levels to below all dopant excited states.

As reported in the March 2008 issue of *Nano Letters* (DOI: 10.1021/nl080195p; p. 1197), the researchers prepared a series of colloidal Mn^{2+} -doped CdSe nanocrystals with diameters in the range of $2 \text{ nm} < \delta < 5 \text{ nm}$ by using a soft chemistry synthesis

approach and measured their absorption and luminescence spectra. It was found that there are two luminescence peaks for small nanoparticles. The higher-energy peak coincides with the first exciton of the CdSe nanocrystals, whereas the lower-energy luminescence peak is attributed to the ${}^6\text{A}_1 \leftarrow {}^4\text{T}_1$ ligand-field transition of Mn^{2+} that is sensitized by CdSe quantum dot (QD) excitation. In contrast, the luminescence spectrum of the larger nanoparticles shows only one major peak, which corresponds to the excitonic emission of CdSe nanocrystals. The photoluminescence results also demonstrate that the energy of the excitonic transition depends on the particle size, but the energy of the Mn^{2+} transition does not. Nanocrystals at diameters of $\sim 3.3 \text{ nm}$ transition between the quenched and unquenched excitonic emission of CdSe nanocrystals.

The large Mn^{2+} -doped CdSe nanocrystals are unique because they show excitonic photoluminescence that is not quenched by the dopants, even though the excitons still interact strongly with the dopants. This was demonstrated using magneto-optical spectroscopies, which confirmed the existence of giant excitonic Zeeman splittings in the CdSe excitonic photoluminescence. In order to define the Zeeman splitting of the as-synthesized Mn^{2+} -doped CdSe nanocrystals, magnetic circular dichroism spectroscopy and magnetic circularly polarized luminescence spectroscopy were measured at low temperature as a function of applied magnetic field. Both techniques show the existence of giant excitonic Zeeman splittings in these diluted magnetic semiconductor (DMS) colloids comparable to those of the best molecular-beam-epitaxy-grown DMS QDs. These results demonstrate spin-polarizable excitonic photoluminescence in these colloidal quantum dots. These kinds of DMS nanocrystals are attractive because they are more processable and more easily handled than analogous materials grown by molecular-beam epitaxy. They therefore introduce new opportunities for studying and applying diluted magnetic semiconductors in nanotechnology including spin-electronic and spin-photon architectures, said the researchers.

ZHAOYONG SUN

Reductive Hydrothermal Synthesis of $\text{LaPO}_4:\text{Ce}^{3+}$, Tb^{3+} Nanophosphors Yields Stronger Photoluminescence Compared with Normal Hydrothermal Method

Rare earth orthophosphates have been widely used as phosphors. Hydrothermal synthesis of rare earth orthophosphates, especially for $\text{LaPO}_4:\text{Ce}^{3+}$, Tb^{3+} (LAP), has

attracted attention due to its low temperature, high homogeneity, high purity, and simplicity. Ce is used as a sensitizer because of the efficient energy transfer between Ce^{3+} to Tb^{3+} . However, oxidation of Ce^{3+} to Ce^{4+} at the hydrothermal stage leads to the loss of luminescence. H. Zhu and co-workers at the Center of Materials Engineering, Zhejiang Sci-Tech University, China, have developed a reductive hydrothermal method by using hydrazine hydrate as a protecting agent, preventing the oxidation of Ce^{3+} to Ce^{4+} , to synthesize high-brightness LAP nanophosphors. The as-synthesized LAP nanophosphors exhibit a high-quenching concentration of Tb^{3+} and the $\text{La}_{0.4}\text{Ce}_{0.4}\text{Tb}_{0.2}\text{PO}_4$ nanophosphor shows almost the same PL intensity as that of the commercial $\text{La}_{0.7}\text{Ce}_{0.2}\text{Tb}_{0.1}\text{PO}_4$ bulk powder.

As reported in the May issue of the *Journal of the American Ceramic Society* (DOI: 10.1111/j.1551-2916.2008.02320.x; p. 1682), the researchers prepared a series of LAP nanophosphors by a normal and a reductive hydrothermal method and $\text{La}_{0.7}\text{Ce}_{0.2}\text{Tb}_{0.1}\text{PO}_4$ bulk powder by a coprecipitation method in order to identify the photoluminescent (PL) properties of LAP synthesized by different methods.

The structures and morphologies of the products were determined using x-ray diffraction (XRD) and transmission electron microscopy (TEM), respectively. All LAP samples synthesized show monoclinic structures and exhibit uniform nanorods 10 nm in diameter and 100 nm in length. The PL emission spectra of LAP nanophosphors synthesized by the reductive hydrothermal method show that the PL intensity of LAP nanophosphors increased with increasing Ce^{3+} and Tb^{3+} concentration. The quenching concentration of the LAP nanophosphors ($\sim 20\%$) is higher than that of its bulk powder. The PL intensity of one typical LAP nanophosphor $\text{La}_{0.85}\text{Ce}_{0.1}\text{Tb}_{0.05}\text{PO}_4$ synthesized by the reductive hydrothermal process is much higher than that of the same formula LAP synthesized by the normal hydrothermal process because the reductant prevented the oxidation of Ce^{3+} to Ce^{4+} , which can reduce the energy transfer between Ce^{3+} and Tb^{3+} . Moreover, $\text{La}_{0.4}\text{Ce}_{0.4}\text{Tb}_{0.2}\text{PO}_4$ shows a similar PL intensity as the $\text{La}_{0.7}\text{Ce}_{0.2}\text{Tb}_{0.1}\text{PO}_4$ bulk powder. The researchers also conducted PL decay measurements of three $\text{La}_{0.7}\text{Ce}_{0.2}\text{Tb}_{0.1}\text{PO}_4$ products of bulk powder, nanophosphor prepared by the reductive hydrothermal method and by the normal hydrothermal method. The result shows that the PL lifetime of bulk powder is longer than that of nanophosphors. In addition, LAP nanophosphors prepared by the reductive